

# Development of SiC Gas Sensor Systems

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# **DEVELOPMENT OF SiC GAS SENSOR SYSTEMS**

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## **ABSTRACT**

Silicon carbide (SiC) based gas sensors have significant potential to address the gas sensing needs of aerospace applications such as emission monitoring, fuel leak detection, and fire detection. However, in order to reach that potential, a range of technical challenges must be overcome. These challenges go beyond the development of the basic sensor itself and include the need for viable enabling technologies to make a complete gas sensor system: electrical contacts, packaging, and transfer of information from the sensor to the outside world. This paper reviews the status at NASA Glenn Research Center of SiC Schottky diode gas sensor development as well as that of enabling technologies supporting SiC gas sensor system implementation. A vision of a complete high temperature microfabricated SiC gas sensor system is proposed. In the long-term, it is believed that improvements in the SiC semiconductor material itself could have a dramatic effect on the performance of SiC gas sensor systems.

## **INTRODUCTION**

Silicon carbide (SiC) has high potential as the electronic semiconductor material for a new family of high temperature sensors and electronics. Silicon carbide can operate as a semiconductor and in conditions under which conventional semiconductors cannot

adequately perform such as at temperatures above 600°C. Silicon carbide also has excellent thermomechanical properties and high thermal conductivity [1]. One area where SiC semiconductor technology can be applied is in chemical sensing. Silicon carbide gas sensors have been in development for a number of years using a range of designs including capacitors [2], transistors [3], and Schottky diodes [4-6]. These sensors have been shown to be highly sensitive to several gases including hydrogen and hydrocarbons making them useful for a range of applications.

Three aerospace applications are of particular interest [7]. The first is the monitoring of emissions from high temperature environments such as combustion systems or chemical processing reactors. In both aeronautic and commercial emissions monitoring applications, the detection of hydrocarbons in a mixed chemical environment can be used to reduce emissions and potentially monitor the efficiency and health of the engine. Further, the monitoring of emissions from chemical processing reactors or on-board experiments associated with Space Shuttle or International Space Station operation can be used to provide early warning if a system is malfunctioning or to enhance the experiment.

A second application is the monitoring of fuel leaks in launch vehicles. Detection of low concentrations of hydrogen and hydrogen-based fuels is important to avoid explosive conditions that could harm personnel and damage the vehicle. Reliable vehicle operation also depends on the timely and accurate measurement of these leaks. Further, measurement of fuel gases such as hydrazine at low concentrations is desired due to their high toxicity and potential to contaminate the environment in the space station.

A third application is fire detection on-board commercial aircraft and space vehicles. Rapid detection and location of a fire is extremely important to avoid catastrophic situations. While existing smoke detectors are able to detect fires, they have a high incidence of false alarms and thus a second, independent method of fire detection to complement conventional smoke detection techniques is required. The measurement of chemical species indicative of a fire is envisioned to help reduce false alarms and improve system safety. While carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>) are important, information derived from other gases such as hydrocarbons is also of interest.

These applications require operation in a variety of conditions: from cryogenic temperature to above 600°C, from inert environments to highly corrosive engine conditions, and from the detection of one gas over a wide concentration range in inert environments to the detection of several gases over more narrow concentration ranges in the presence of interfering gases. The sensor design and sensing approach depends strongly on the specific application. Further, supporting technologies like interconnects and packaging, without which the sensor would be inoperable, need to be tailored for the application. A complete, operational sensor system includes not only the sensor itself but also includes supporting electronics, micromachined components, packaging and interconnects. For many applications, the sensor system components would be required to reliably function over long operational lifetimes. While this may be less problematic for

predominately room temperature applications like leak detection, the challenges are considerable in high temperature applications such as engine monitoring.

This paper will give an overview of the on-going technology development at NASA Glenn Research Center (GRC) to produce SiC-based gas sensor systems for a range of aeronautic and industrial applications. This includes not only the development of the sensor but also the supporting technologies that make the sensor system operational in a given environment. First, an overview of the sensor development will be given. Then a review of the state of development of enabling technologies necessary for SiC sensor systems is presented including: 1) Supporting high temperature SiC electronics, 2) High temperature contacts, 3) Micromachining technologies, and 4) High temperature packaging. The use of the SiC-based sensor in engine environments as part of a High Temperature Electronic Nose will be discussed. A vision of how these individual components can be integrated into a SiC gas sensor system will be presented. While work proceeds towards improving long-term durability at high temperatures and realizing the high potential of these systems, SiC gas sensor systems are still operational for a range of lower temperature applications. One significant future direction of this work is improvements in the starting SiC semiconductor material.

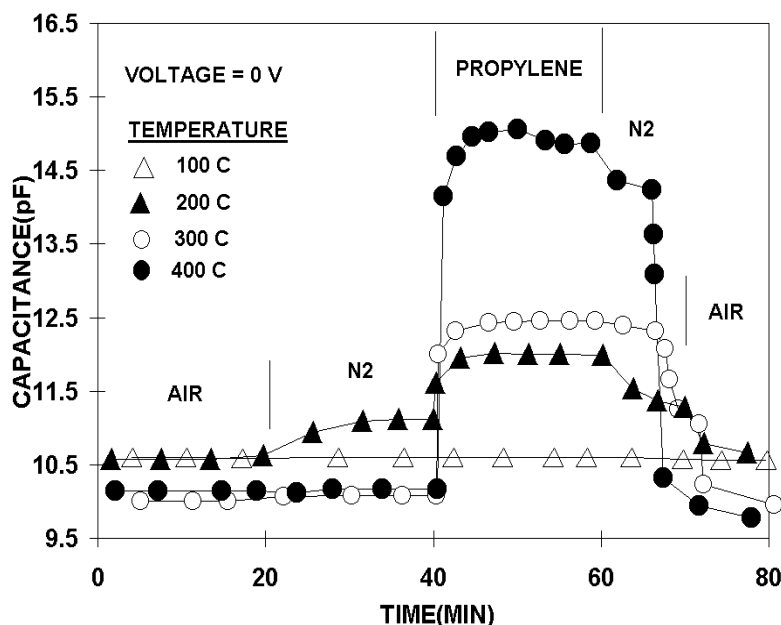
## **SENSOR DEVELOPMENT**

The development of SiC gas sensors at NASA GRC has centered on the development of a stable, gas-sensitive SiC-based Schottky diode. A Schottky diode is composed of a metal in contact with a semiconductor (MS) or a metal in contact with a very thin insulator or oxide on a semiconductor (MIS or MOS). For gas sensing applications, the metal is often a catalytic film. The advantage of a Schottky diode sensing structure in gas sensing applications is its high sensitivity. This is especially useful in applications such as emission measurements where the concentrations to be measured are low (on the order of ppm). The detection mechanism for hydrogen ( $H_2$ ) involves the dissociation of  $H_2$  on the surface of a catalytic metal leading to the formation of a dipole layer at the interface of the metal and the insulator (or metal-semiconductor interface depending on the structure). This dipole layer affects the effective Schottky barrier height of the diode resulting in an exponential change in the forward current and a quadratic change in the capacitance [8-9] while the diode is under bias. The detection of hydrocarbons is possible if the sensor is operated at a high enough temperature to dissociate the hydrocarbon and produce atomic hydrogen. The resulting atomic hydrogen affects the sensor output in the same way as molecular hydrogen [4, 10-11].

The Schottky diode structure under development at NASA GRC began with palladium (Pd) thin film on SiC MS structures (Pd/SiC). Direct contact between the catalytic metal and the semiconductor allows changes in the catalytic metal to have maximum effect on the electrical properties of the Schottky diode. The details of this work are reviewed elsewhere [4]. The sensor detects hydrogen and hydrocarbons in inert or oxygen containing environments. Figure 1 illustrates one main advantage of SiC over silicon (Si) semiconductors in Schottky diode hydrocarbon sensing applications [4].

The zero bias capacitive response of a Pd/SiC Schottky diode to one hydrocarbon, propylene, over a range of temperatures is shown. The sensor operational temperature is increased from 100°C to 400°C in steps of 100°C and the response of the sensor is observed. At a given temperature, the sensor is exposed to air for 20 minutes, N<sub>2</sub> for 20 minutes, 360 ppm of propylene in N<sub>2</sub> for 20 minutes, N<sub>2</sub> for 10 minutes, and then 10 minutes of air. The magnitude of sensor response to 360 ppm propylene depends strongly on the operating temperature. A sensor operating temperature of 100°C is too low for propylene to dissociate on the Pd surface, so the device does not respond at all. The three other curves for 200°C, 300°C, and 400°C show that elevating the temperature increases the sensor's response to propylene. The presence of propylene can be detected at any of these higher temperatures with 200°C being the minimum operating temperature determined in this study. Since the operating temperature of Si Schottky diodes is typically confined below 200°C, these results demonstrate the significant advantages of using SiC diodes rather than Si diodes in some gas sensing applications.

Figure 1. The temperature dependence of the zero bias capacitance to various gas mixtures for a Pd/SiC Schottky diode.



However, the sensor response is adversely degraded by extended high temperature heating. Prolonged heating at 425°C has been shown to change the sensor properties and to decrease sensor sensitivity [4]. The reason for this change in diode properties is thought to be due to reactions between the Pd and SiC at the interface upon heating causing disruption of the metal structure due to oxygen (O<sub>2</sub>) and Si [12-13]. Efforts are underway to stabilize the sensor structure for long-term, high temperature operation.

Two structures have been demonstrated to improve the stability of the Pd-based Schottky diode structure over that of the simple Pd/SiC Schottky sensor [5]. The first structure involves the incorporation of chemically reactive oxides into the SiC-based Schottky diode structure. A wide variety of materials, e.g. metal oxides such as SnO<sub>2</sub>, are sensitive to hydrocarbons (C<sub>x</sub>H<sub>y</sub>) and nitrogen oxides (NO<sub>x</sub>) at high temperatures.



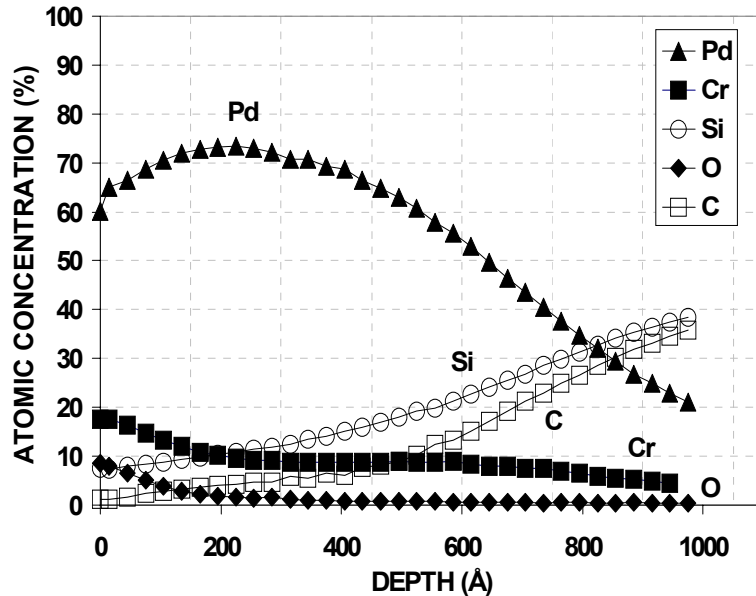
These materials could be incorporated as a sensitive component into MOS structures. Unlike silicon, SiC-based devices can be operated at high enough temperatures for these materials to be reactive to gases such as hydrocarbons ( $C_xH_y$ ) and nitrogen oxides ( $NO_x$ ). This results in a different type of gas sensitive structure: a metal reactive-oxide semiconductor structure (MROS). The advantages of this type of SiC-based structure include 1) increased sensor sensitivity since the diode responds to gas reactions due both the catalytic metal and the reactive oxide, 2) improved sensor stability since the gas reactive oxide can act as a diffusion barrier layer between the metal and SiC potentially stabilizing the sensor's interfacial properties, and 3) the ability to vary sensor selectivity by varying the composition of the reactive oxide element enabling the fabrication SiC-based arrays for high temperature gas detection. (See Summary and Future Directions discussion below).

The second structure is PdCr directly deposited on SiC (PdCr/SiC). The advantages of PdCr as a high temperature alloy have been explored extensively in strain gage applications [14]. It is a stable high temperature material able to provide static strain measurements at temperature up to 1100°C. However, its use in a gas-sensing SiC-based structure depends on not only its inherent stability but also on such factors as the alloy's reactivity to SiC and the catalytic interactions of PdCr alloy with the gases to be measured. Results have been presented previously which suggest that PdCr can form a stable system that has high sensitivity to hydrogen (~4 orders of magnitude change for 120 ppm  $H_2$  in  $N_2$  at 100°C) even after 240 hours of heating at 425°C in air [5]. The results of surface and interface analyses indicated that after testing (or heating) part of PdCr thin film was still clean (free of Si) and the sensor surface was also relatively clean (lower silicon oxides contents) compared with those of Pd/SiC sensors examined [15]. It was suggested that a carbide component at the interface region may be critical in maintaining sensor performance stability and sensitivity.

However, despite these promising results, the ability to systematically produce films with combined stability and sensitivity has been problematic. One potential reason for this is the lack of consistency of the SiC surface (See Summary and Future Directions discussion below and reference 1). Recent results have shown that PdCr films of various Pd/Cr ratios show varying levels of reactivity with the SiC surface as well as sensor drift after extended durations at high temperature. A representative Auger depth profile is shown in Figure 2 of a PdCr film heated at 450°C for 100 hours and periodically exposed (an average of at least 20 minutes every 24 hours) to 0.5% hydrogen in nitrogen. Two major trends have been found to correspond to a decline in sensor response: Pd migration into the SiC interface to form of palladium silicides ( $PdSi_x$ ) and the subsequent migration of elemental silicon to the surface from the SiC. Palladium silicides are present throughout the film and the Si on and near the surface oxidizes forming silicon dioxide. Accompanying this silicide and oxide formation are the migration of carbon (C) into the PdCr from the SiC and of Cr into the SiC. In summary, significant migration of the components of the PdCr/SiC interface occur with high temperature heating. Similar silicide and oxide formations have been noted in Pd/SiC diodes heated at 425°C [12]. Thus, the use of the PdCr alloy alone on SiC is not sufficient to produce stable and

sensitive sensors. Control of the migration of the constituents of the PdCr/SiC including Pd, Si, and Cr as well as the subsequent formation of silicides and oxides is necessary to achieve improved stability.

Figure 2. AES depth profile of a representative PdCr/SiC diode after periodic 0.5% hydrogen in nitrogen gas exposure for 100 hrs at 450 °C.



In order to stabilize these films at higher temperatures, various approaches have been investigated. A combination of thin film layering, thermal pre-treatment, and surface coating of the SiC substrate has been used. One approach involves the deposition of multilayer thin films deposited on n-type, C-face 6H-SiC substrates with a 3  $\mu\text{m}$  epilayer obtained from Cree Research [16]. The sample was cleaned and pretreated with a thiol compound prior to metal layer depositions. The thin film combination of Pd (175 Å)/Cr(35 Å)/PdCr(13%)[410 Å]/Cr(70 Å) was deposited via sputtering using an argon plasma at pressures in the mTorr range. The wafer was diced and a sample was treated at 450°C by cyclically varying the ambient between, air, nitrogen, and exposure (while biased) to hydrogen at a concentration of 0.5% in a balance of nitrogen gas. Auger depth profiling was performed on both an as-deposited and treated film. Further details of the sample preparation and analysis is planned for a future publication.

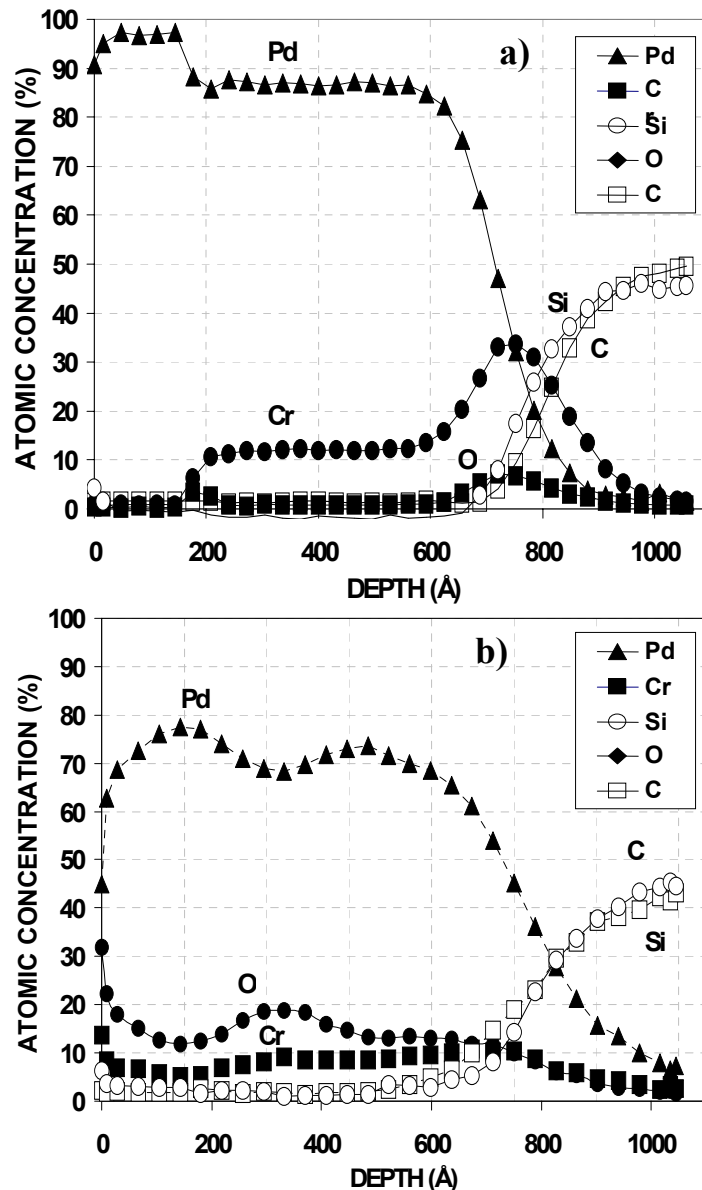
The results of the AES analysis of an as-deposited film are shown in Figure 3 for the as-deposited as well as that for a treated film. In both curves, the inflection point in the Si and C profile curves occurs at about 800 Å and the width of the interfacial region is nearly invariant. This indicates a thermally stable interface even though limited interfacial diffusion of Pd, Cr, and O occurred. In the as-deposited film, the various Pd, Cr, and Pd Cr layers are defined by rapid changes in the elemental composition with slight broadening of the Cr distribution near the interface. After treatment, Pd and Cr redistribute throughout the film. Palladium and Cr have a nearly uniform distribution in the film while Pd has only a slightly enhanced concentration at the interface and into the SiC. The AES data for the Si region definitively shows that the migrated Pd species is

metallic and no evidence of any silicide was found even on the surface where significant  $\text{SiO}_2$  had previously formed. Oxygen distributes through the film and to some degree through the interface. An accumulation of Cr/Cr oxide species near the surface is not observed. It should be noted that this approach has apparently eliminated oxygen 'leaching' of Cr from the PdCr alloy film.

Figure 3. AES depth profile of the Pd/Cr/PdCr(13%)/Cr annealed sensing film:

a) as deposited.

b) after annealing at  $450^\circ\text{C}$  for approximately 100 hrs with periodic hydrogen gas exposure.



Thus, a combination of thin film layering and surface treatment of the SiC substrate has been effectively employed to improve the stability of PdCr sensing films on SiC substrates especially with respect to Si migration. Even after over 100 continuous hours at  $450^\circ\text{C}$ , the metal-SiC interface remains predominantly intact and Si migration to the surface is not observed. Further, Cr accumulation at the surface is also eliminated.

This behavior is in stark contrast to that of the PdCr/SiC sample seen in Figure 2. The data suggests that treatment of the surface with the thiol compound decreases the chemical potential of the surface below that for the untreated SiC surface and reduces the Pd and Cr silicide formation. However, preliminary sensor response testing suggests that, while less Si diffusion has taken place, this sample may have significantly reduced sensitivity compared to that discussed in, for example, reference 5.

Further efforts are underway to produce a SiC Schottky diode sensor that is both stable and sensitive at high temperatures. However, it should be noted that even though the sensor drifts at temperatures such as 450°C, this does not preclude its use at lower temperatures for some applications. While some applications require high temperature exposure (e.g., in-situ engine monitoring) or some gases need higher temperatures to decompose for detection (e.g., methane), other applications are less demanding and thus may be open for use of this sensor in its present stage of development. Further, if the application only requires short operation times, then use of the present sensor is feasible. (See High Temperature Electronic Nose discussion below for a limited duration demonstration of the SiC-based gas sensor.)

## **ENABLING TECHNOLOGIES**

The long-term goal is to establish a complete SiC-based gas sensor systems able to meet the needs of a range of applications. The most challenging applications are those that require in-situ measurements in harsh environments e.g. aeronautic or commercial engine applications. However, even applications which do not normally require harsh environment operation may want the system to remain operational if the environment becomes harsh e.g., fire detectors which operate at room temperature may need to be continuously operational after a fire breaks out and the temperature rises considerably. The following is a discussion of the state of maturity of some of the enabling technologies meant for harsh environment applications that would support the SiC-based gas sensor and contribute to a complete sensor system. For more moderate applications, other technologies may be used and even preferred for cost reasons.

### High Temperature Electronics

Silicon carbide presently appears to be the strongest candidate semiconductor for implementing 500 to 600°C integrated electronics in the nearer term [1]. SiC electronics are envisioned to enable signal conditioning and wireless communication and thus could be used to complement SiC gas sensor technology in this temperature range. Discrete SiC devices such as pn junction diodes, junction field effect transistors (JFET's), and metal-oxide-semiconductor field effect transistors (MOSFET's) have previously demonstrated excellent electrical functionality at 600°C for relatively short time periods [1]. However, for such electronics to be useful in high temperature applications, much longer 600°C harsh-environment lifetimes must eventually be realized. The operational lifetime of SiC-based transistors at 600°C is not limited by the semiconductor itself, but is instead largely governed by the reliability and stability of various interfaces with the SiC crystal surface. The physical degradation of the metal-semiconductor ohmic contact interface

limits the 600°C operating lifetime of all devices, while high temperature MOSFET operating lifetime is also limited by the electrical integrity of the oxide-semiconductor interface. Thus, junction-based transistors without gate insulators appear more feasible in the nearer term. Of the candidate junction-based transistor technologies that might be used to implement SiC integrated circuits, the pn junction gate JFET seems closest to demonstrating long-term operation at 600°C.

An example of the maturity of the JFET technology is the demonstration of 600°C digital logic using SiC JFET's [17]. A resistive load direct-coupled FET logic (DCFL) approach was adopted to demonstrate simple 600°C digital logic using SiC JFET's. The non-planar epitaxial gate JFET design was adopted in favor of a planar ion-implanted structure, largely to alleviate the challenging process of sufficiently activating high-dose  $p^+$  ion implants in SiC. A two-level interconnect approach using oxidation-resistant silicon nitride as the dielectric passivant along with oxidation resistant gold for the metal interconnect also adopted. Figure 4 shows operation of NAND gate at 600°C. The devices show good operation at these high temperatures as shown in the figure. These circuits are the fundamental building blocks of more complex systems and therefore the capability of building high temperature circuits to complement SiC gas sensor technology potentially exists. However, degradation of contacts to the device in Figure 4 limited operational circuit testing at 600°C to less than one hour.

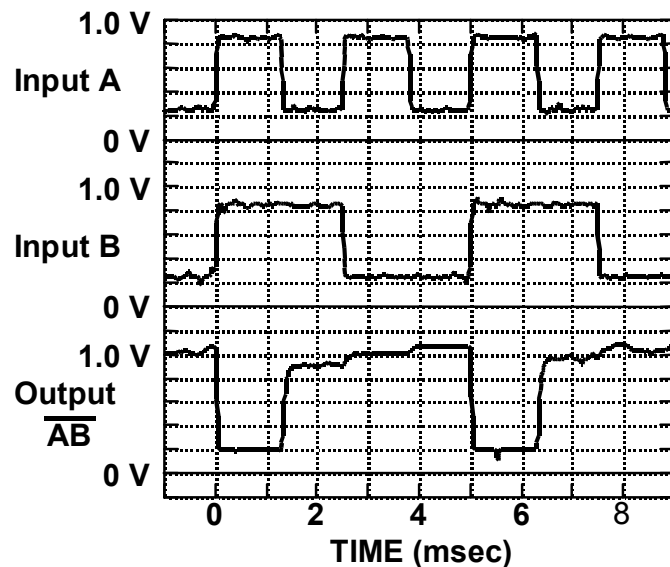


Figure 4. NAND gate test waveforms at 600°C with  $V_{DD} = 2.5$  V,  $V_{SS} = 0$  V,  $V_{\text{substrate}} = -1.4$  V.

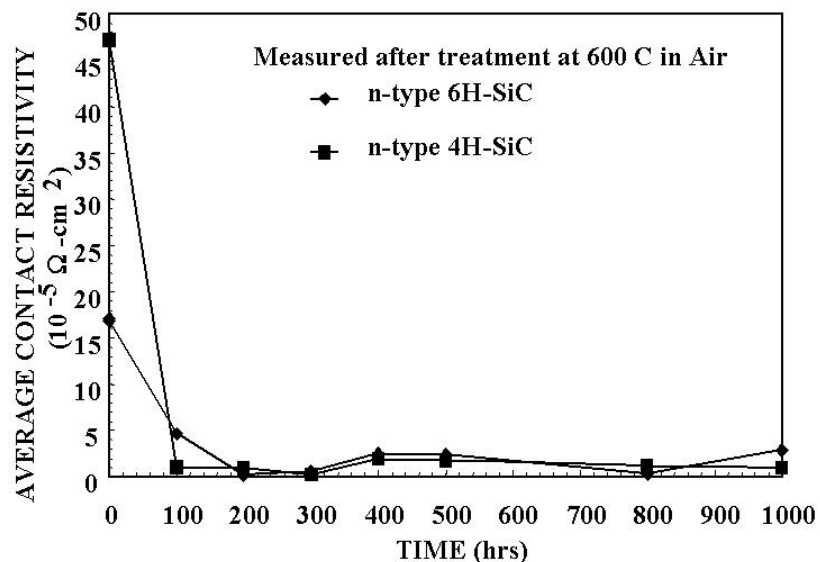
#### High Temperature Contacts

The operational lifetime of circuits operated at 600°C could be extended by using separately optimized n-type and p-type ohmic contacts specifically designed to resist high-temperature degradation. Significant progress has been made in improving the reliability of high temperature contacts [18]. A multilayer approach using Ti (100nm)/TaSi<sub>2</sub> (200nm)/Pt(300nm) on n-type 6H-SiC players has resulted in a thermally stable ohmic contact metallization at temperatures up to 600°C. These contacts exhibited linear ohmic

characteristics with contact resistance in the range of  $(0.3 \times 10^{-4} - 8 \times 10^{-4} \Omega\text{-cm}^2)$  on n-type epilayer doped between  $0.6$  to  $2 \times 10^{19} \text{ cm}^{-3}$ . AES was used to analyze the metal and semiconductor interfaces to understand the prevailing reactions. The thermal stability of the ohmic contacts between  $500^\circ\text{C}$  and  $600^\circ\text{C}$  in air is believed to be due to the formation of silicides and carbides of titanium after being annealed during a pretreatment at  $600^\circ\text{C}$  in  $\text{H}_2$  (5%)/ $\text{N}_2$  forming gas for 30 minutes. The oxidation of Si species that migrated after  $\text{TaSi}_2$  decomposition is the most probable diffusion barrier mechanism.

This metallization approach has been demonstrated to result in thermally stable ohmic contact at  $600^\circ\text{C}$  in air for 1000 hours as seen in Figure 5 where the average specific contact resistivity is shown for both 6H and 4H samples. The Ti/ $\text{TaSi}_2$ /Pt contacts have low resistivity and high stability after an initial break-in period. Therefore, a metallization scheme exists to improve the durability of SiC electronics for up to 1000 hours at  $600^\circ\text{C}$ . Future work will demonstrate this contact technology in integrated SiC electronics circuits. Given the high stability of this metallization system, an obvious approach to resolution of the gas sensor stability/sensitivity issues discussed above might be the use this metallization scheme as a gas sensor. However, preliminary results have suggested that this system is generally not sensitive to hydrogen and hydrocarbons.

Figure 5. Average specific contact resistivity of Ti/ $\text{TaSi}_2$ /Pt contacts as a function of heat treatment at  $600^\circ\text{C}$  for both 6H and 4H samples.



### Micromachining Technology

The use of micromachining in chemical sensors has several advantages. By combining micromachining technology with microfabrication techniques, three-dimensional chemical sensing structures can be formed. In Si, the sacrificial layer method is often used [19]. The sacrificial layer method employs a deposited underlayer that can be selectively removed chemically. This results in a suspended diaphragm structure with a small thermal mass on which the sensor, temperature detector and heater can be fabricated. This yields a sensor structure with higher thermal stability, minimal heat loss, and less energy consumption. Figure 6 shows the use of a diaphragm in the structure in

an oxygen sensor design. The fabrication of this structure depends on chemical anisotropic etching of Si. In order to achieve such a design in SiC, controlled etching processes for SiC are necessary.

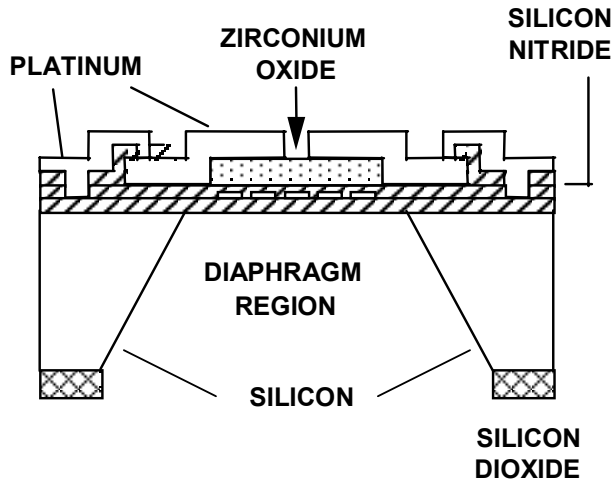


Figure 6: The structure of a microfabricated amperometric oxygen sensor based in Si showing a diaphragm structure.

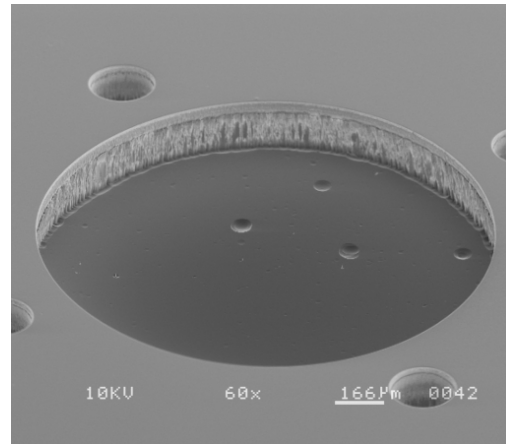


Figure 7: Scanning Electron Microscopy (SEM) micrograph of cavity etched in 6H-SiC by deep reactive ion etching method.

However, the fabrication of a diaphragm structure using chemical etching in SiC is problematic [1,20]. Due to the chemical inertness of SiC, standard etching processes are ineffective. A deep RIE process using an inductively coupled plasma (ICP) etch system has been developed which provides anisotropic etch profiles and smooth etched surfaces, a high rate (2200 Å/min), and a high selectivity (55:1) to the nickel etch mask. This results of this process are shown in Figure 7 where a cavity is etched in SiC with an etch depth of 245 µm. Further work is needed to optimize the surface cleaning procedure which precedes the deep etch process. In addition, work is planned to develop a process which produces smoother sidewalls, which are important in some applications, such as for mesas for vertical structure high-voltage devices. Nonetheless, the fabrication of this cavity, intended for pressure sensing applications, demonstrates the base capability to perform deep SiC semiconductor etching. As application needs arise for minimizing the thermal mass of SiC gas sensor structures, the same type of technology could be used to fabricate diaphragm structures for SiC gas sensing applications.

### High Temperature Packaging

The operation of chemical sensors in high temperature environments requires packaging technologies beyond those of conventional device packaging technology. For example, for *in situ* engine monitoring of chemical species, sensors must operate at temperatures of at least 500°C and at gas turbine pressures up to 3000 pounds per square inch (psi). This is a chemically reactive gas environment composed of chemical species such as oxygen in air, and hydrocarbons/hydrogen in fuel, and species such as NO<sub>x</sub> in the

combustion products. Additionally, the sensors and associated electronics may be exposed to vibration. Thus, the packaging materials and basic components must withstand temperatures of at least 500°C, chemical corrosion, and potentially high dynamic pressure and high acceleration. These packaging components include the substrate, metallization material(s), electrical interconnections within the package (such as wire-bond), and die-attach. These requirements are far beyond standard operation conditions for most advanced (commercial) packaging and thus new technology development is necessary.

The most promising technology for such applications are ceramic substrates combined with precious metal thick-film metallizations. These technologies have been proposed for hybrid [21] and chip-level packaging of high temperature operable microsystems [22] based on their excellent stabilities at high temperature and in chemically reactive environments. Aluminum nitride was proposed to package high temperature SiC MEMS because this material possesses a low thermal expansion coefficient which is close to that of SiC [22-23].

An innovatively designed, fabricated, and assembled chip-level electronic package for high-temperature harsh environment microelectronic systems using ceramic (aluminum nitride and aluminum oxide) substrates and gold (Au) thick-film metallization (see Figure 8) has been produced. The electrical interconnection system of this advanced packaging system, including the thick-film metallization and wirebond, has been successfully tested at 500°C in an oxidizing environment for over 5000 hrs. A compatible low resistance die-attach scheme using Au thick-film material as a conductive bonding material has also been developed to package SiC microsystems.

This complete electrical interconnection system was tested using an NASA GRC fabricated SiC semiconductor test chip (Schottky diode with a gold contact) in an oxidizing environment in a temperature range from room temperature to 500°C for more than 1000 hrs. The thick-film-based interconnection system demonstrated the required low (2.5 times of the room-temperature resistance of the Au conductor) and stable (3 percent decrease in the first 1500 hrs of continuous test) electrical resistance at 500°C in an oxidizing environment. Also, the electrical isolation impedance between the printed wires that were not electrically joined by a wirebond remained satisfactorily high ( $>0.4 \text{ G}\Omega$ ) at 500°C in air. The attached SiC diode demonstrated low ( $< 3.8 \times 10^{-2} \text{ }\Omega\text{-cm}^2$ ) and relatively consistent forward resistance from room temperature to 500°C, as shown in Figure 8. This implies the operability of the die-attach between room temperature and 500°C. Preliminary results from finite element analysis of a SiC die-attach with  $1\text{mm}^2$  die on an aluminum nitride substrate show low thermal stress [24]. These results indicate that this prototype package and the compatible die-attach scheme meet the basic requirements for low-power, long-term operation in high-temperature and chemically reactive environments. This base technology can be then tailored for individual chemical sensing applications. For example, the package design shown in Figure 8 seals the device. This approach is appropriate for electronic devices to support the chemical sensors, while a chemical sensor package would expose the sensor itself.



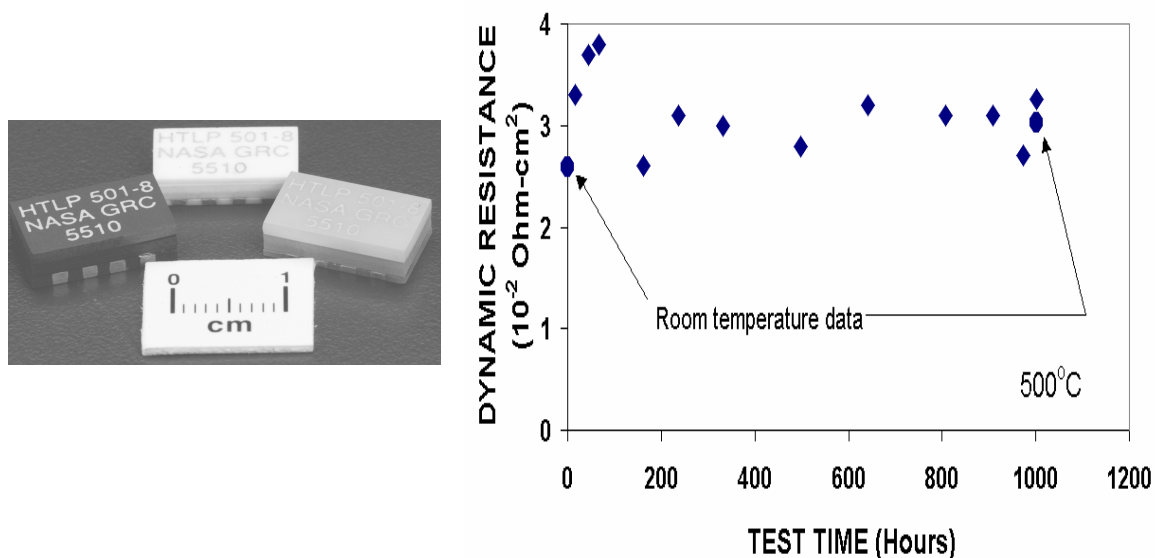


Figure 8. a) Prototype high-temperature electronic package composed of ceramic substrates and Au thick-film metallization for harsh environment systems. b) Forward resistance of a packaged SiC Schottky diode characterized at 500°C in oxidizing environment for over 1000 hrs.

### SiC GAS SENSOR APPLICATION: HIGH TEMPERATURE ELECTRONIC NOSE TECHNOLOGY

An example of the integration of SiC gas sensors into a system is the inclusion of the sensor in the High Temperature Electronic Nose. The function of the High Temperature Electronic Nose is to characterize the chemical signature of the emissions in a complex high temperature chemical environment. The characterization of such an environment is difficult with a single sensor due to issues of sensor selectivity and cross-sensitivity [7]. Rather, an array of sensors optimized for selectivity to specific gases is necessary for the characterization of the components of a mixed environment containing, for example,  $C_xH_y$ ,  $O_2$ , and  $NO_x$ . Development of a High Temperature Electronic Nose consisting of such a microfabricated gas sensor array combined with data processing software and operable at high temperatures and high flow rates would be a dramatic step towards realizing the goal of monitoring/control of emissions produced by an engine, a power generation unit, or a chemical reactor.

The elements necessary for the High Temperature Electronic Nose include those that have been discussed in this paper (although not all the components are presently high temperature compatible). A SiC Schottky diode gas sensor is included in this array; its output signal is complemented by other microfabricated sensors to allow differentiation of several gases. This microfabricated array is mounted into a package and placed in the high temperature environment. Interconnections are then made from the sensor array to standard electronics mounted outside of the hot area where the Nose operates.

The electronics process the signals from the sensors as well as control their temperatures with heaters and temperature detectors. In the future, this gas response will be integrated and interpreted using neural net processing, currently being developed by Ohio State University to allow a more accurate determination of the chemical constituents of harsh, high temperature environments.

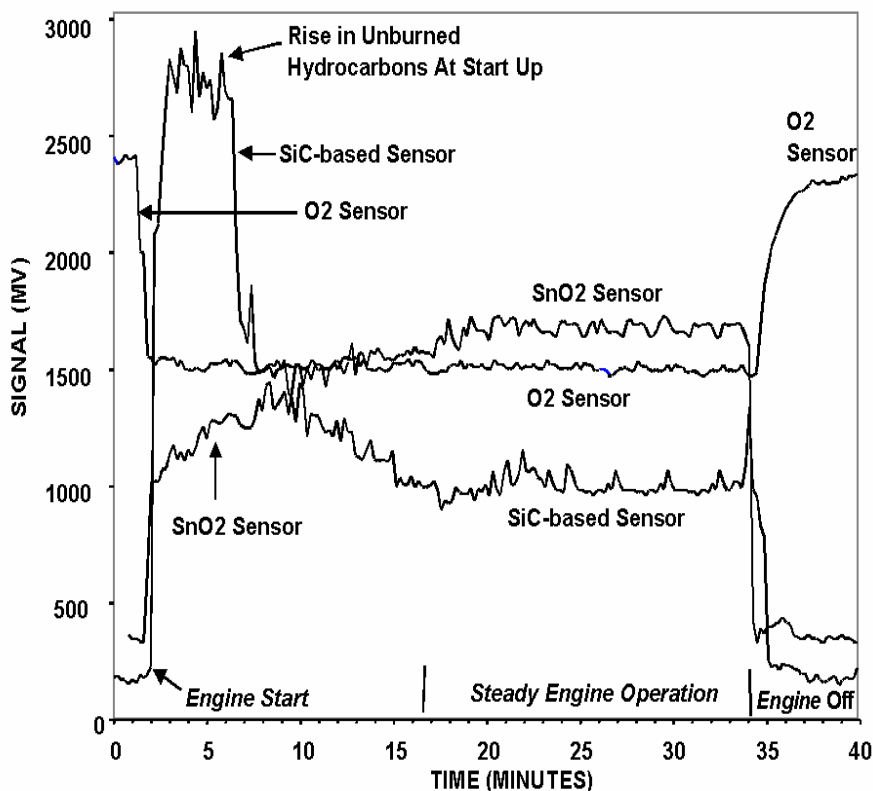


Figure 9. The response of a sensor array composed of a SiC-based hydrocarbon sensor, a tin oxide based sensor (doped for NO<sub>x</sub> sensitivity), and an oxygen sensor.

This first generation High Temperature Electronic Nose has been demonstrated on a modified automotive engine [25]. Figure 9 shows the response of a SiC-based (C<sub>x</sub>H<sub>y</sub>) sensor, tin oxide based sensor (doped for NO<sub>x</sub> sensitivity), and an O<sub>2</sub> sensor at various engine operation stages. The figure shows the individual sensor responses during the initial start of the engine, a warm-up period, a steady state operation period, and at the engine turn-off. The sensors were operated at 400°C while the engine operating temperature was 337°C. Each sensor has a different characteristic response. The oxygen sensor shows a decrease in O<sub>2</sub> concentration while the NO<sub>x</sub> and C<sub>x</sub>H<sub>y</sub> concentrations increase at start-up. The hydrocarbon concentrations decrease as the engine warms up to steady-state while the NO<sub>x</sub> concentration increases before stabilizing. The O<sub>2</sub>, NO<sub>x</sub>, and C<sub>x</sub>H<sub>y</sub> concentrations all return to their start-up values after the engine is turned off. These results are qualitatively consistent with what would be expected for this type of engine. They also show the value of using sensors with very different sensing mechanisms in an electronic nose array: the information provided by each sensor was unique and monitored a different aspect of the engine's chemical behavior.

## SUMMARY AND FUTURE DIRECTIONS

This paper has presented an overview of the status of development of the components of a potential SiC gas sensor system operable at high temperatures. While the system would have to be tailored for the given application, an envisioned SiC-based gas sensor system for high temperature, harsh environments could include the following components: A Schottky diode-based gas sensor for highly sensitive detection with, depending on the application, complementary sensors for different gases and concentration ranges. For example, gas sensitive resistors could be included on the same SiC substrate for higher concentration measurements while sensors of significantly different operating principles could be combined with the SiC gas sensors (High Temperature Nose approach) to characterize mixed chemical environments. The SiC gas sensors themselves can be tailored for the application by using different types of alloys or MROS structures for improved sensitivity. Physical sensors (such as pressure sensors) could also be included depending on the application. SiC electronics could be integrated with sensors for signal conditioning and onsite data processing. Wireless communication would eliminate the need for wires (although for a truly wireless system, on-board power would also be necessary). The sensor structure would be micromachined for minimal thermal mass and power consumption and include an integrated temperature detector and heater for temperature control. High temperature packaging would allow system operation in harsh environments with sufficient protection for the high temperature electronics while allowing the exposure of the sensors to the operational environment.

The components of this system are in various stages of maturity as discussed in this paper. The SiC-based gas sensor has shown promise but long-term, high temperature operation is still problematic. Lower temperature operation of these sensors is still a viable option for a number of applications. The contact and packaging technologies have been shown to be reliable at high temperatures for extended periods with micromachining capabilities available. The electronic device technology operational lifetime can be enhanced by the improved contact and packaging technologies. Further development will be necessary before these electronics can be integrated into a SiC-based gas sensor system to provide data processing and communication. In the meantime, remote location of components such as electronics, as demonstrated with the High Temperature Electronic Nose, is a viable option until complete integrated systems can be fabricated for high temperature, harsh environments.

However, the technology advancement which may have the strongest impact on the maturation of SiC gas sensor systems (sensor and enabling technologies) is improved SiC electronic materials. Compared to silicon wafer standards, present-day SiC wafers are small, expensive, and generally of inferior quality. In addition to high densities of crystalline defects such as micropipes and closed-core screw dislocations, commercial SiC wafers also exhibit significantly rougher surfaces, and larger warpage and bow than is typical for silicon wafers [26]. Further, problems with the quality of the oxide growth on SiC have prevented realization of Metal-Oxide-Semiconductor Field Effect Transistors (MOSFET) technology in SiC. The vast majority of semiconductor integrated

circuit chips in use today in silicon rely on MOSFET technology. The disparity is not surprising considering that silicon technology has undergone several decades of commercial process refinement. While significant advances have nonetheless been made in the development of SiC sensors and electronics, the existence of improved SiC starting material is expected to significantly enhance the development of these technologies.

Recent work has been aimed at improving the quality of the SiC starting material on which devices are fabricated by eliminating the defects and growing superior SiC surfaces on device-sized mesas. The formation of SiC mesa surfaces as large 0.2 by 0.2 mm completely free of a single atomic step was recently reported [27]. Work is presently on-going to take advantage of the properties of these step-free surfaces in a manner that could enable advantageous new electrical devices to be realized and the realization of complete, harsh environment SiC gas sensor systems.

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